United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-83-016 April 1983

EPA

Project Summary

Effects of Organic Solvents on the Permeability of Clay Soils

K. W. Brown and D. C. Anderson

This laboratory study examines the suitability of using water alone to test the permeability of compacted clay liners of hazardous landfills and surface impoundments. Traditional permeability tests using water alone qualified four clay soils for lining hazardous waste facilities on the basis of low permeabilities (1 x 10^{-7} cm sec^{-1}). But these same clays underwent large permeability increases when tested with basic, neutral polar, and neutral nonpolar organic fluids. They also showed potential for substantial permeability increases when exposed to concentrated organic acids.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Knowledge of the permeability-- a main criterion used to judge whether a compacted soil liner will prevent movement of leachates below or adjacent to a disposal facility--is needed to determine a liner's suitability for use as a containment system. However, little information is available concerning the impact of waste fluids on the permeability of clay liners. Also, no simple permeability test method has been developed that is suitable for use with a range of possible waste fluids.

The report begins with a brief state-of-the-art review of the use of clay liners in hazardous waste landfills and surface impoundments. The review examines the physical classes of fluid-bearing hazardous wastes, the leachates they generate, and the predominant fluids in these leachates. Available information is also summarized on native soils used to construct compacted clay liners.

A description is then given of the comparative permeability testing that was conducted with four compacted clay soils and a wide range of possible waste fluids. Potential interactions between waste fluids and clay liners are evaluated, and the permeability of typical clay soils is examined.

State-of-the-Art Review

Overview

RCRA regulations concerning hazardous waste disposal facilities (effective November 19, 1981) prohibit the landfill disposal of drums containing free liquids. Furthermore, the regulations prohibit the disposal of bulk liquids in hazardous waste landfills unless the landfill has an "adequate liner" and a "leachate collection and removal system."

Hazardous wastes placed in landfills can be categorized into the following four physical classes: aqueous-inorganic, aqueous-organic, organic, and sludges. This categorization was used, for example, in a report to Congress in 1974.

Leachate Generated by Hazardous Waste

Two leachates should be investigated to determine the effects of a waste on the permeability of a liner. The first, or primary leachate, is made up of all the flowable constituents of the waste--the fluids (solvents) and the dissolved components (solutes). The secondary leachate is that generated from water percolating through a disposal facility, and it consists of water, the waste solvent, and the solutes.

The solvent phase of the leachate usually has the greatest impact on clay liner permeability. However, nearly all literature describing the permeability of clay liners consider water only as the leachate. Water is viewed as the carrier fluid, and organic chemicals are considered to be present only in trace quantities. Such is not always the case, however, since many wastes have an organic fluid phase.

In addition to the fluid and dissolved phases of leachates, a suspended phase may also be present (e.g., inorganic pigments suspended in an organic fluid saturated with paint).

Fluids in Hazardous Waste Leachate

Organic fluids may be classified into four groups: Organic acids, organic bases, neutral polar organics, and neutral nonpolar organics. The most important fluid property affecting soil permeability is viscosity. Any slow-viscosity fluid is leachate and able to extract organic components from otherwise dry waste.

Organic Acids

Organic acids are organic fluids with acidic functional groups such as phenols and carboxylic acids. These fluids may react with the dissolved clay soil components through a variety of mechanisms. Anaerobic decomposition byproducts are an ever present source of organic acids in waste impoundments.

Organic Bases

Though it is not clear whether organic bases can dissolve certain components of clay minerals, they have been implicated in dissolving clay liners. Adsorption of organic bases by clays is rapid and nearly irreversible, and it yields a porous matrix that is structurally stable under either aqueous or organic fluid flow.

Neutral Polar Organics

Polar compounds compete with water for adsorption sites on the negatively charged clay surfaces. The adsorption of an organic fluid to clay changes the behavior of the latter, including possibly its permeability. Examples of such polar compounds are alcohols, aldehydes, ketones, glycols, and alkyl halides.

Neutral polar organic fluids tend to reduce the surface tension of water, and hence the viscosity. The decreased viscosity would significantly increase the permeability of a soil when measured with that fluid.

Neutral Nonpolar Organics

Neutral nonpolar organic fluids have low water solubilities and little polarity with which to compete with water for adsorption sites on clay minerals. In the presence of hydraulic gradient, however, nonpolar fluids move downward through a clay without being appreciably attenuated by clay minerals. Examples of nonpolar organic fluids are aliphatic and aromatic hydrocarbons.

Water

Water strongly adsorbs to clay surfaces in multiple layers and forms large hydration spheres around inorganic soil cations. Because of these properties, certain clay soils swell and seal upon hydration and shrink and crack when water is displaced or extracted. Clay surfaces of a liner are initially water-wet. But if a percolating organic fluid has a higher affinity for the clay surface than does water, the clay may become organic-wet. Since the clay surface is negatively charged, polar or positively charged components of organic leachates will have an affinity for interlayer surfaces of an expandable lattice clay. The water solubility of an encroaching fluid will improve its access to the clay surface since water on the clay surface may be several layers thick.

Components of Clay Soils

A clay soil is a porous mixture of air, water, organic matter, and inorganic minerals. Approximately 40% of the clay soil by volume is pore space (occupied by air and water) and 60% is solids. Of the solids, trace amounts to 15% is organic matter, and 85% to 99% or more is organic minerals. The inorganic minerals include sand (0.05 to 2.0 mm), silt-sized rock fragments (0.02 to 0.05 mm), and at least 35% clay-sized particles (0.002 mm). These clay-sized particles consist of rock fragments smaller than silt and a variety of clay minerals.

Pore space in clay soils is largely determined by the structural arrangements of solid soil components. Pore-size distribution determines the permeability of clay soils to fluids.

Solid components that dominate the behavior of clay soils are organic matter, clay minerals, and cations adsorbed to clay minerals. Organic matter generally imparts structure to clay soil and results in larger pores and higher permeability. But the low permeability usually associated with clay soils is due largely to characteristics of clay minerals and associated cations.

Soil organic matter consists of partially decomposed plant and animal residues and humus. The addition of organic matter can transform clay soils with normally low permeabilities into highly pervious soils. For example, organic wastes have been added to farmland for centuries to improve the soil structure, but the addition of organic sludges to clay soils at hazardous wasteland treatment facilities may destroy the long-term integrity of clay liners.

The mineral fraction of native clay soils and subsoils is usually of mixed composition. Several clay mineral species are normally present, with one or two species dominating. Four of the most widespread species are 2:1 expandable layer smectites, 2:1 nonexpandable layer illites, 1:1 nonexpandable layer kaolinites, and multiple form 1:1 halloysites.

Exchangeable cations are positively charged ions that are reversibly adsorbed to negatively charged clay surfaces. Both the composition of exchangeable cations and the resulting equilibrium concentration of the cations in soil water will greatly affect the permeability of a compacted clay soil.

Failure Mechanisms of Clay Liners

Failure mechanisms of clay liners are defined here as any interaction of the compacted clay soil liner that can substantially increase its permeability. Climatological cycles (wet-dry, freeze-thaw, etc.) are widely understood to cause much of the structural development and permeability increases in clay soils. Our main concern here, however, is to investigate the little understood inservice environments of remolded and compacted clay soil liners used for hazardous waste landfills and surface impoundments. The main failure mechanisms studied in this context are (1) dissolution and piping and (2) volume changes.

Dissolution and Piping

Dissolution and piping have complimentary effects on clay liner permeability, so they are considered together. As a dissolving agent erodes pore walls, the released fragments of soil tend to clog pores unless they are piped out of the compacted clay soil. Piping is the active erosion of soil from below the ground surface that results from substratum pressure and the concentration of seepage in localized channels.

Both organic and inorganic acids and bases react with and often dissolve portions of compacted clay soils. Acids dissolve aluminum, iron, and silica, which erodes the lattice structure of clays and releases undissolved fragments for migration with a percolating leachate. Acids may also oxidize native organic matter and dissolved calcium carbonate nodules.

Pore sizes of compacted clay soils are not usually large enough to transport slaked fragments produced by reactive acids or bases. Thus pore clogging and at least a temporary decrease in clay liner permeability will result. But if the clay liner is placed atop strata containing pores large enough to pipe soil fragments, or if the clogging fragments are dissolved, permeability increases can eventually occur.

Volume Changes

Volume changes occur in clay soils from bulk and interlayer shrinkage. Bulk shrinkage can usually be identified by visual inspection for cracks, fissures, joints, faults, slickensides, shears, channels, ice wedges, planes, and chambers. Interlayer shrinkage is manifested by shifts in pore size distribution and may not be detected visually, but its impact on clay liner permeability can be just as dramatic.

Volume changes in clay liners occur when there is a change in the water content of clay. Such changes may occur if an organic leachate extracts water from the clay liner. The magnitude of volume change depends on the clay mineral type, arrangement of clay particles, size of clay particles, surface area per unit weight of clay, and the kind and proportion of cations adsorbed to the clay.

Swelling of compacted clay soils is a complex result of many interacting mechanisms. Swelling is related to the presence of clay minerals, organic compounds adsorbed to clay surfaces, and exchangeable cations and to fabric or structural arrangement of clay particles, overburden pressure, and Atterberg limit values of clay soils. Though swelling tends to decrease permeability of clay soils, it simultaneously indicates potential for shrinkage if the soil environment is substantially altered.

Interlayer spacing of clay minerals refers to spacing between adjacent basal surfaces. Changes in interlayer spacing of clay may affect its bulk volume, pore size distribution, and thus permeability. Factors affecting this spacing include the clay mineralogy, properties of the fluid, and the exchangeable cations adsorbed to the clay minerals.

Permeability Measurements of Clay Soils

Because of the large variety of waste fluids placed in hazardous waste landfills and impoundments, there is great need for a qualitative permeability test that can rapidly determine potential effects of waste fluids on the permeability of clay liners. Such a test should use standardized procedures and readily available equipment to simplify training of laboratory personnel and to allow intercalibration by independent laboratories. The test method developed for this study was designed to meet these objectives.

The permeability tests conducted for this study do not attempt to reproduce typical field conditions and are not suitable for exact determinations of field permeability values. But they are useful for performing rapid comparative studies to evaluate the potential influence of waste fluids on permeability of compacted clay soil liners.

Materials and Methods

Five steps were followed to provide a basic perspective on the permeability of clay liners to organic fluids:

1. Delineation of physical classes of organic liquid-bearing hazardous wastes.
2. Description of leachates generated by various waste classes.
3. Interpretation of the types of fluid contained by various waste leachates.
4. Evaluation of characteristics of clay soils used to line disposal facilities.
5. State-of-the-art review of mechanisms of interaction between organic fluids and clay soils that may alter the permeability of clay liners.

Data gathered during these phases of the study were then used as guides for choosing clay soils and methods for comparative permeability studies.

Fluids Studied

Seven organic fluids and water were selected for the comparative permeability studies. The four classes of these organic fluids were acidic, basic, neutral polar, and neutral nonpolar.

All organic fluids used in this study were reagent grade (pure), whereas actual waste leachates are normally a mixture of fluids combined with various organic and inorganic solutes. Also, waste leachates often contain suspended particles that could clog or coat soil pores. This study used pure fluids to eliminate variables other than fluid properties that could effect the resulting permeability values.

Glacial acetic acid represented the acidic organic fluid class, and aniline stood for the basic organic fluids. Three neutral polar organic fluids (methanol, acetone, and ethylene glycol) were chosen along with two neutral nonpolar organic fluids (heptane and xylene). Water (0.01N $CaSO_4$) was used as a control fluid to establish the baseline permeability of each soil core.

Clay Soils Studied

Four native clay soils with diverse mineralogical or chemical properties were selected for this study. Two of the soils (noncalcareous smectite and calcareous smectite) had predominantly smectitic clay minerals but different chemical properties. The two other soils (mixed cation kaoliniate and mixed cation illite) contained predominantly kaolinitic and illitic clay minerals, respectively. In addition, each soil was characterized by the following:

1. Permeability of less than 1 x 10^{-7} cm sec^{-1} when compacted at optimum water content.
2. Geographic extent of at least 1 million ha.
3. Deposits thick enough to permit economical excavation for use as clay liners.
4. Minimum clay mineral content of 35% by weight.

After collection the clay soils were broken into clods the size of golf balls and airdried. The soils were then ground sufficiently to pass through an ASTM No. 4 sieve (4.75 mm) and stored at room temperature in large drums before testing.

Permeability Test Considerations

Steps were taken to minimize sources of error in soils of low permeability (leaks, trapped air, volatile losses, and turbulent flow or channeling along the soil chamber wall) and to eliminate inherent dangers associated with organic fluids under pressure. Other steps were taken to ensure accurate permeability values, including increasing the hydraulic gradient to reduce the time needed for testing and to minimize trapped air.

Procedures

Compacted soil cores were used to evaluate permeability to organic fluids. These were prepared at or above optimum water content. After compaction, the soil cores were mounted on permeameter base plates and fitted with fluid chambers and permeameter top plates (Figure 1). Each top plate was then fitted with a pressure inlet connecting it to a pressurized air source via the pressure distribution manifold (Figure 2).

After the soils were seated at low pressure, the selected air pressure was applied to the permeameter fluid chamber until stable permeability values were obtained with the standard leachate. Pressure was then released, and permeameters were disassembled. The core was next examined for signs of swelling or deterioration.

Any soil that had expanded out of its mold was removed with a straight edge, ovendried, and weighed to estimate the percent of swelling. Additional standard leachate was then passed through the three soils that had swollen to ensure that permeability was not affected by the excess soil removal.

Next, the remaining standard leachate was removed and replaced with the organic fluids for all but the control permeameter. After passage of 0.5 to 2.0 pore volumes of organic fluids, the permeameters were depressurized and disassembled, and the cores were dissected to determine whether structural changes had occurred in the compacted clays. Curves for organic fluid breakthroughs were determined simply by measuring the organic fluid volume (with immiscible fluids) or by thermoconductivity gas chromatography (with miscible fluid).

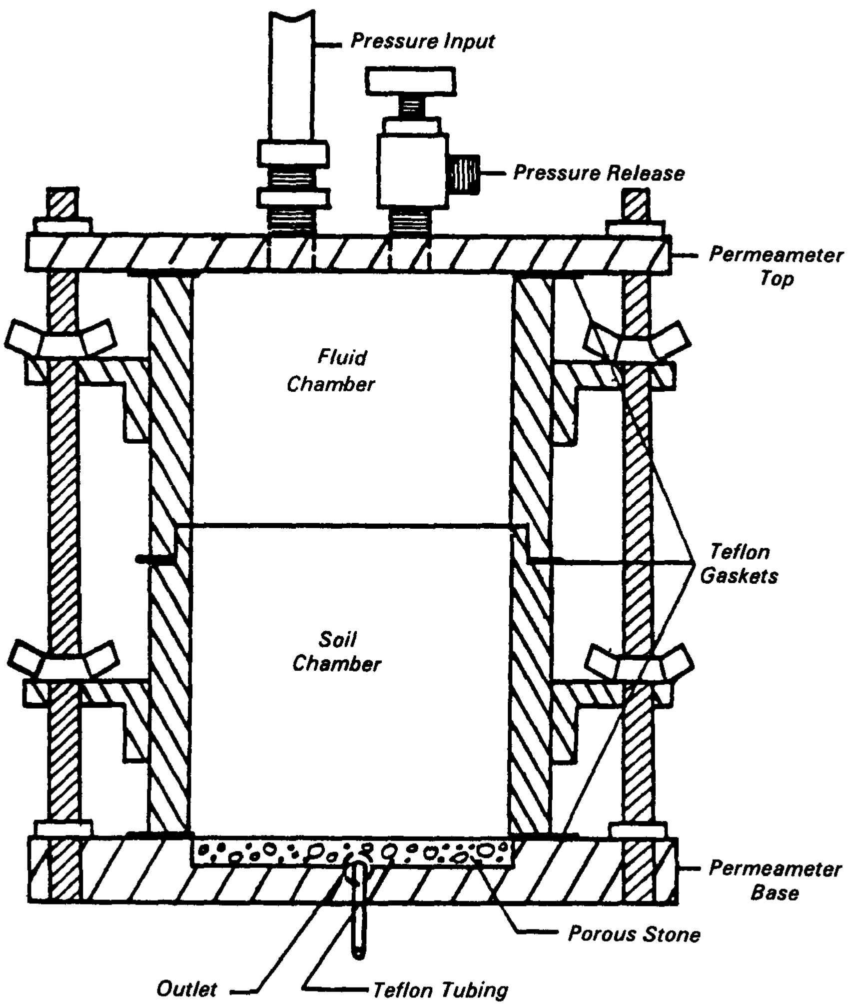

Figure 1. Schematic of the compaction permeameter.

Results and Discussion

Relative Performances of the Four Clay Soils

When the four soils used in this study were evaluated with the traditional permeability test using water (0.01 N $CaSO_4$), the resultant permeabilities were lower than 1 x 10^{-7} cm sec^{-1}. But these same clay soils underwent large increases in permeability when basic, neutral polar, and neutral nonpolar organic fluids were used in place of water. They also showed the potential for substantial permeability increases when exposed to concentrated organic acids. Permeability data are summarized in Table 1.

Of the four clay soils studied, the noncalcareous smectitic clay showed the lowest initial permeability but the least resistance to increases in permeability when exposed to organic fluids. The calcareous smectitic clay had intermediate initial permeability, but it showed a much greater resistance to permeability changes than its noncalcareous counterpart. The result was that the noncalcareous clay generally had a higher final permeability than the calcareous smectitic clay. In addition, of the two smectitic clay soils, the noncalcareous tended to yield organic fluids in the effluent after less fluid had passed through the soil.

Though the kaolinitic clay soil had the highest initial permeability of the four soils studied, it nearly always showed the greatest resistance to permeability changes. Organic fluids generally appeared in the effluent of this soil after passage of greater fluid volumes than with the illitic or noncalcareous smectitic clay soils.

The illitic clay soil had both intermediate initial permeability and resistance to permeability changes. But the organic fluids tended to appear in the effluent of the illitic clay soil after passage of less fluid than with the other clay soils.

Overall, the kaolinitic and calcareous smectitic clay soils performed best of the four clays studied. These two clays showed greater resistance to permeability increases, and organic fluids appeared in their effluent after passage of more fluid (larger pore volume values) than the illitic or noncalcareous smectitic clay soils. Note, however, that all four clay soils showed permeabilities greater than 1 x 10^{-7} cm sec^{-1} when exposed to several of the organic fluids tested.

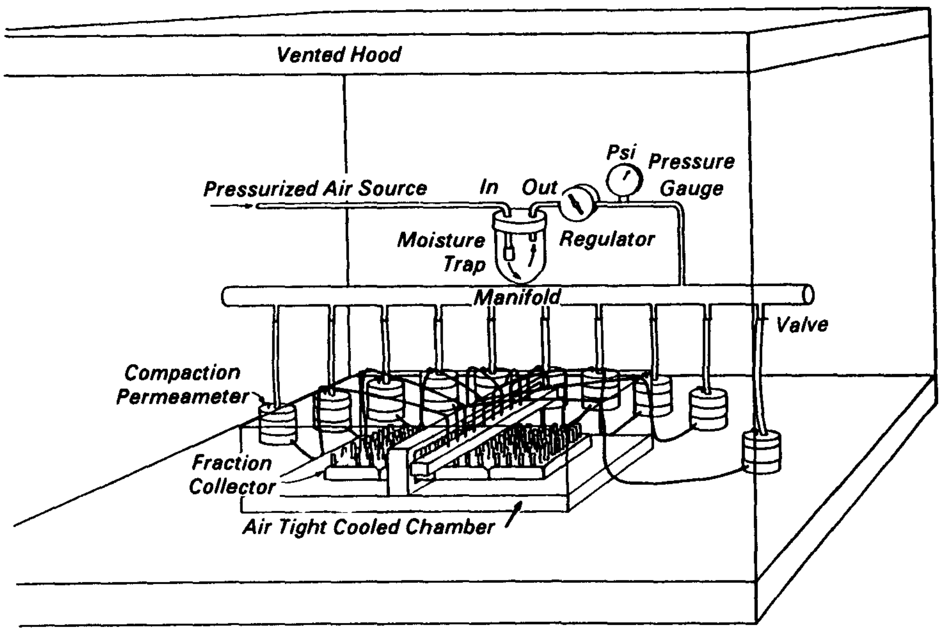

Figure 2. *Schematic of the compaction permeameter test apparatus.*

Relative Effects of Organic Fluids on Permeability of Clay Soils

Organic acids apparently affect permeability by mechanisms that are different from those of other organic fluids studied. The operative mechanisms for permeability changes with acetic acid appeared to be dissolution of soil particles followed by piping of the particle fragments through the soil. A sharp initial permeability decrease resulted as the migrating particle fragments clogged the fluid-conducting pores. But permeability then increased gradually (with two of the soils) as acid dissolved the soil particles that clogged the pores.

No dissolution or piping was observed for the soils permeated by the weak organic base (aniline) or the neutral organic fluids. These fluids tended to cause permeability increases by altering the structural fabric of the soil.

Neutral nonpolar fluids caused initial permeability increases of approximately two orders of magnitude. The soils so treated tended, however, to reach relatively constant permeability at that point. The basic and neutral polar fluids showed continuous permeability increases with no apparent tendency to reach maximum values. Though the large viscosity of ethylene glycol and aniline slowed the

Table 1. *Permeability of Four Clay Soils to Water (0.01N $CaSO_4$)**

	Permeability (cm sec^{-1})			
Fluids to Which the Soil Column Would be Exposed	*Noncalcareous Smectite*	Calcareous Smectite	Mixed Cation Kaolinite	Mixed Cation Illite
Water (0.01N $CaSO_4$)	*2.14(±0.26) x 10^{-9}*	*7.77(±0.64) x 10^{-9}*	*1.92(±0.18) x 10^{-8}*	*6.07(±3.88) x 10^{-9}*
Acetic Acid	*1.59(±0.19) x 10^{-9}*	*6.48(±0.11) x 10^{-9}*	*1.30(±0.35) x 10^{-8}*	*7.31(±0.93) x 10^{-9}*
Aniline	*2.91(±0.23) x 10^{-9}*	*3.86(±0.19) x 10^{-9}*	*1.51(±0.12) x 10^{-8}*	*3.87(±1.62) x 10^{-9}*
Ethylene Glycol	*1.39(±0.14) x 10^{-9}*	*4.67(±0.64) x 10^{-9}*	*1.55(±0.35) x 10^{-8}*	*6.75(±1.52) x 10^{-9}*
Acetone	*1.14(±0.10) x 10^{-9}*	*3.47(±0.66) x 10^{-9}*	*2.01(±0.12) x 10^{-8}*	*3.06(±0.69) x 10^{-9}*
Methanol	*1.55(±0.17) x 10^{-9}*	*5.07(±0.52) x 10^{-9}*	*1.46(±0.42) x 10^{-8}*	*5.54(±1.52) x 10^{-9}*
Xylene	*1.44(±0.21) x 10^{-9}*	*5.62(±0.11) x 10^{-9}*	*1.77(±0.15) x 10^{-8}*	*3.51(±1.13) x 10^{-9}*
Heptane	*1.51(±0.13) x 10^{-9}*	*3.62(±0.37) x 10^{-9}*	*1.87(±0.10) x 10^{-8}*	*4.26(±0.99) x 10^{-9}*
All Permeameters	*1.63(±0.50) x 10^{-9}*	*4.98(±1.60) x 10^{-9}*	*1.71(±0.25) x 10^{-8}*	*5.14(±2.20) x 10^{-9}*

**Values for individual columns represent mean ± one std. dev. of 2-7 permeability measurements.*
Values given under the designation "All Permeameters" represent mean ± one std.dev. for all soil columns of a given soil type.

rate at which these fluids increased permeability relative to the less viscous acetone and methanol, all four fluids increased the permeability of soils as compared with values obtained with water (0.01 N $CaSO_4$).

The full report was submitted in fulfillment of Grant No. R806825010 by Texas A&M University under the sponsorship of the U.S. Environmental Protection Agency.

K. W. Brown and D. C. Anderson are with Texas A&M University, College Station, TX 77845.

***Robert E. Landreth** is the EPA Project Officer (see below).*

The complete report, entitled "Effects of Organic Solvents on the Permeability of Clay Soils," (Order No. PB 83-179 978; Cost: $16.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

☆U. S. GOVERNMENT PRINTING OFFICE:1983/659-095/1936

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335

Official Business
Penalty for Private Use $300

RETURN POSTAGE GUARANTEED

[redacted]

PS 0000329
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604